J. Org. Chem. **2000,** *65,* 8105−8107

Hexacarbonyldiplatinum(I) Cation-Catalyzed Carbonylation of Olefins in Concentrated Sulfuric Acid

Qiang Xu,* Masahiro Fujiwara, Mutsuo Tanaka, and Yoshie Souma

Osaka National Research Institute, AIST, MITI,
Midorigaoka, Ikeda, Osaka 563-8577, Japan

xu@onri.go.jp

Received June 9, 2000

Introduction

Since the discovery of the first metal carbonyls, $Pt(CO)_2Cl_2$, $Pt(CO)Cl_2$, and $Pt_2(CO)_3Cl_4$, by Schützenberger in 1870,[1] metal carbonyl complexes have played a very important role in chemistry and the chemical industry.[2] For the typical metal carbonyls such as $Ni(CO)_4$, $Co_2(CO)_8$, and $Mn(CO)_4{}^{3-}$, the average vibrational frequencies, ν(CO), are considerably lower than the value for free CO, 2143 cm^{-1}, mainly due to the strong metal-to-CO π-back-bonding.[3] Reactions catalyzed by such metal carbonyls usually require high temperature and high pressure.[2]

Recently, there has been a rapid development in the preparation and structural characterization of homoleptic metal carbonyl cations and their cationic derivatives ranging from groups 6 through 12,[4,5] which, in contrast to the typical metal carbonyl complexes, have a distinguishing characteristic in that the CO vibrational frequencies are significantly increased; they have remarkably reduced π-back-bonding and reactive CO ligands. Metal carbonyl cations have been employed as active catalysts under very mild conditions. Cu(I), Ag(I), Au(I), Pd(I), and Rh(I) carbonyls have been shown to be highly active for the catalytic carbonylation of olefins in strong acids at atmospheric pressure of CO.[6−8] $[Pt(CO_4)][Sb_2F_{11}]_2$ has recently been used for the stereospecific tetramerization of 2-propynol and the polymerization of arylacetylenes.[9]

Platinum catalysts have been used in many important reactions, such as the hydroformylation and hydrosilylation of unsaturated compounds.[2,10] In this paper, we report the first example of the homoleptic, dinuclear, cationic metal carbonyl catalyst, i.e., hexacarbonyldiplatinum(I), $[\{Pt(CO)_3\}_2]^{2+}$, in concd H_2SO_4, with which olefins react with CO to produce tertiary carboxylic acids in high yields at atmospheric pressure and room temperature.

Results and Discussion

Formation of $[\{Pt(CO)_3\}_2]^{2+}$ (1) and *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$ (2) in Concentrated Sulfuric Acid. The first homoleptic Pt(II) carbonyl complex, $[Pt(CO)_4][Pt(SO_3F)_6]$, was isolated by the reductive carbonylation of $Pt(SO_3F)_4$ in HSO_3F with CO at 25 °C.[11d] This reaction represents the partial reduction of Pt(IV) by CO. Increasing the reaction temperature from 25 °C to 80 °C results in complete reduction to $Pt(CO)_2(SO_3F)_2$,[11a,b] via the yellow intermediate, $[Pt(CO)_4][Pt(SO_3F)_6]$. It has been reported that in SbF_5, the creamy white $Pt(CO)_2(SO_3F)_2$ complex can be readily converted to the thermally stable, white salt, $[Pt(CO)_4][Sb_2F_{11}]_2$, in the presence of a CO atmosphere.[11c]

We have found that hexacarbonyldiplatinum(I), $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), the first homoleptic, dinuclear platinum(I) carbonyl cation, is formed in concd H_2SO_4 under a CO atmosphere according to eq 1:[12]

$$2\mathrm{Pt}^{\mathrm{IV}}\mathrm{O}_2 + 9\mathrm{CO} + 2\mathrm{H}^+ \xrightarrow[\text{rt, 1 atm}]{\text{concd } \mathrm{H_2SO_4}} \underset{\mathbf{1}}{[\{\mathrm{Pt}^{\mathrm{I}}(\mathrm{CO})_3\}_2]^{2+}} + 3\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \qquad (1)$$

This involves a greater degree of reduction of Pt(IV) than has been observed in superacids and must result from the use of a less acidic medium. The reductive carbonylation of PtO_2 by CO takes ca. 2 weeks in concd H_2SO_4 at room temperature and atmospheric pressure to go to completion and produce a colorless solution of **1**. Prolonged (ca. 1 day) evacuation of the solution of **1** in concd H_2SO_4 results in disproportionation and the ex-

---

* To whom correspondence should be addressed. Phone: +81-727-51-9652, Fax number: +81-727-51-9629.

(1) (a) Schützenberger, P. *C. R. Hebd. Seances Acad. Sci.* **1870**, *70*, 1134. (b) Schützenberger, P. *C. R. Hebd. Seances Acad. Sci.* **1870**, *70*, 1287. (c) Schützenberger, P. *Bull. Chim. Fr.* **1870**, *14*, 97.

(2) For leading references, see: (a) Falbe, J., Ed. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980. (b) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds;* Plenum Press: New York, 1991.

(3) (a) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1991**, *94*, 2031. (b) Pierloot, K.; Verhulst, J.; Verbeke, P.; Vanquickenborne, L. G. *Inorg. Chem.* **1989**, *28*, 3059. (c) Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1980**, *19*, 1805. (d) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 1619.

(4) (a) Bernhardt, E.; Bley, B.; Wartchow, R.; Willner, H.; Bill, E.; Kuhn, P.; Sham, I. H. T.; Bodenbinder, M.; Bröchler, R.; Aubke, F. *J. Am. Chem. Soc.* **1999**, *121*, 7188. (b) Bröchler, R.; Freidank, D.; Bodenbinder, M.; Sham, I. H. T.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1999**, *38*, 3684. (c) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402.

(5) (a) Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Organometallics* **1999**, *18*, 3769. (b) Luppinetti, A. J.; Strauss, S. H. *Chemtracts-Inorg. Chem.* **1998**, *11*, 565. (c) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.

(6) For a recent review, see: Xu, Q.; Souma, Y. *Top. Catal.* **1998**, *6*, 17.

(7) (a) Souma, Y.; Sano, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3296. (b) Souma, Y.; Sano, H. *J. Org. Chem.* **1973**, *38*, 3633. (c) Souma, Y.; Sano, H.; Iyoda, J. *J. Org. Chem.* **1973**, *38*, 2016.

(8) (a) Xu, Q.; Nakatani, H.; Souma, Y. *J. Org. Chem.* **2000**, *65*, 1540. (b) Xu, Q.; Souma, Y.; Umezawa, J.; Tanaka, M.; Nakatani, H. *J. Org. Chem.* **1999**, *64*, 6306. (c) Xu, Q.; Imamura, Y.; Fujiwara, M.; Souma, Y. *J. Org. Chem.* **1997**, *62*, 1594.

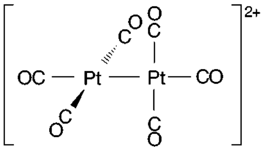
(9) Weber, L.; Barlmeyer, M.; Quasdorff, J.-M.; Sievers, H. L.; Stammler, H.-G.; Neumann, B. *Organometallics* **1999**, *18*, 2497.

(10) (a) Bhaduri, S.; Mukesh, D. *Homogeneous Catalysis: Mechanisms and Industrial Applications*; Wiley-Interscience: New York, 2000. (b) Cornils, B.; Herrmann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compunds*; Wiley-VCH: Weinheim, 2000.

(11) (a) Ahsen, B. v.; Wartchow, R.; Willner, H.; Jonas, V.; Aubke, F. *Inorg. Chem.*, submitted for publication. (b) Hwang, G.; Wang, C.; Bodenbinder, M.; Willner, H.; Aubke, F. *J. Fluorine Chem.* **1994**, *66*, 159. (c) Hwang, G.; Wang, C.; Aubke, F.; Willner, H.; Bodenbinder, M. *Can. J. Chem.* **1993**, *71*, 1532. (d) Hwang, G.; Bodenbinder, M.; Willner, H.; Aubke, F. *Inorg. Chem.* **1993**, *32*, 4667.

(12) (a) Xu, Q.; Heaton, B. T.; Jacob, C.; Mogi, K.; Ichihashi, Y.; Souma, Y.; Kanamori, K.; Eguchi, T. *J. Am. Chem. Soc.* **2000**, *122*, 6862. (b) Xu, Q.; Souma, Y.; Heaton, B. T.; Jacob, C.; Kanamori, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 208.

10.1021/jo000883c CCC: $19.00



1

Figure 1. Schematic structure of hexacarbonyldiplatinum(I) cation, $[\{Pt(CO)_3\}_2]^{2+}$ (**1**).

clusive formation of the nearly colorless complex, *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$ (**2**), according to eq 2:

$$\mathbf{1} \underset{+\,4CO/concd\ H_2SO_4}{\overset{-\,4CO/concd\ H_2SO_4}{\rightleftarrows}} \underset{\mathbf{2}}{cis\text{-}Pt(CO)_2{}^{2+}{}_{(solv)}} + Pt^0 \qquad (2)$$

This observation indicates that the CO ligands are more weakly bound to Pt(I) in **1** than to Pt(II) in **2**, but more tightly bound than in the Cu(I), Ag(I), Au(I), and Rh(I) carbonyl cations which require only brief evacuation to reversibly remove the CO ligands.[6,8] A very slow reformation of **1** occurs upon reintroduction of CO to a solution of **2**. **1** has been completely characterized by NMR (^{13}C and ^{195}Pt), IR, Raman, and EXAFS spectroscopy.[12] The structure of **1** is rigid on the NMR time scale at room temperature. The strongly polarized, sharp Raman band at 165 cm^{-1} (ρ = ca. 0.25) indicates the presence of a direct Pt−Pt bond. The IR and Raman spectra in the CO stretching region are entirely consistent with the presence of only terminal CO's on a nonbridged Pt−Pt bond with D_{2d} symmetry (see Figure 1). The average CO stretching vibrational frequency, $\nu_{av}(CO)$, for **1** is 2199 cm^{-1}, higher than 2143 cm^{-1}, the value for free CO.[13] EXAFS measurements show that the Pt−Pt bond is 2.718 Å, and the mean length of the Pt−C bonds is 1.960 Å. The mean Pt−C distance of 1.960 Å is longer than that found for *cis*-$Pt(CO)_2(SO_3F)_2$ (1.882 Å);[11a] this is consistent with the observation that the CO ligands are more weakly bound to Pt(I) in **1** than to Pt(II) in **2** since evacuation of **1** results in the formation of **2** through the loss of CO. The geometric optimization for **1** by a density functional calculation at the B3LYP level of theory predicts that the dinuclear cation contains two essentially planar tricarbonyl platinum(I) units that are linked via a Pt−Pt bond about which they are twisted by exactly 90.0° with respect to each other (Figure 1).[12,14]

Hexacarbonyldiplatinum(I) Cation-Catalyzed Carbonylation of Olefins. Platinum catalysts, which work in both homogeneous and heterogeneous systems, have assumed a very important position in synthetic chemistry and the chemical industry.[2,10] For example, platinum(II) hydrides catalyze the hydroformylation of olefins to selectively give the straight chain products.[2,15] Platinum complexes have been employed as active catalysts (Speier's catalyst) for the hydrosilylation of unsaturated compounds.[10,16]

Table 1. Hexacarbonyldiplatinum(I) Cation-catalyzed Carbonylation of Olefins in Concd H_2SO_4[a]

substrate	*tert*-carboxylic acid	yield/%[b]
1-pentene	2,2-dimethylbutanoic	70
	others	1
1-hexene	2,2-dimethylpentanoic	49
	2-methyl-2-ethylbutanoic	23
	others	1
1-octene	2,2-dimethylheptanoic	43
	2-methyl-2-ethylhexanoic	20
	2-methyl-2-propylpentanoic	11
	others	2
1-decene	2,2-dimethylnonanoic	39
	2-methyl-2-ethyloctanoic	20
	2-methyl-2-propylheptanoic	11
	2-methyl-2-butylhexanoic	3
	others	2
cyclohexene	1-methylcyclopentanecarboxylic	55

[a] PtO_2/substrate = 2.0 mmol/5.0 mmol, 96% H_2SO_4 10 mL, CO 1 atm, rt. [b] Based on substrate.

The Koch reaction, another carbonylation, gives tertiary carboxylic acids in strong acids such as H_2SO_4, HF, H_3PO_4, or $BF_3{\cdot}H_2O$, in which no metal catalysts are used but high CO pressure is necessary.[17] In strong acids, an olefin is protonated to form a carbocation intermediate, which isomerizes to a *tert*-carbocation via the Wagner−Meerwein rearrangement.[18] The protonation of the isomerized olefins is in equilibrium with the deprotonation of the carbocation.[19] Polymerization of the olefins and carbocations also occurs as a competing reaction in this system. In the original Koch reaction, the direct reaction of the carbocations with the dissolved CO in the solution leads to the formation of acylium cations, which react with water to give tertiary carboxylic acids. Without cationic metal carbonyl catalysts, olefins are carbonylated to form the carboxylic acids in yields as low as 10% under atmospheric pressure of CO and at room temperature due to the low CO solubility in the solution and the presence of the polymerization as a competing reaction.

It has been reported that cationic Cu(I), Ag(I), Au(I), Pd(I), and Rh(I) carbonyl catalysts cause the Koch-type reaction to proceed under very mild conditions.[6−8] This paper reveals the first example of the homoleptic, dinuclear, cationic metal carbonyl catalyst, $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), with which olefins readily react with CO to give *tert*-carboxylic acids in high yields at room temperature and atmospheric pressure (eq 3). As shown in Table 1, the addition of the hexacarbonyldiplatinum(I) cation (**1**) drastically enhances the rate of carbonylation, which is completed in 1 h, and *tert*-carboxylic acids are formed in high yields. The selectivities of the *tert*-carboxylic acids by **1** are similar to those of the cationic Cu(I) or Au(I) carbonyl catalyst;[6−8] for example, a 2:1 mixture of 2,2-dimethylpentanoic acid and 2-methyl-2-ethylbutanoic acid and a 4:2:1 mixture of 2,2-dimethylheptanoic acid, 2-methyl-2-ethylhexanoic acid and 2-methyl-2-propylpentanoic acid were obtained from 1-hexene and 1-octene, respectively. The catalytic activity of **1** is close to that of

---

(13) Herzberg, G. *Spectra of Diatomic Molecules*; 2nd ed.; van Nostrand: New York, 1950.

(14) Mogi, K.; Sakai, Y.; Sonoda, T.; Xu, Q.; Souma, Y. *J. Mol. Struct.*, submitted for publication.

(15) Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

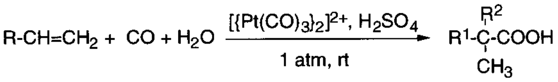
(16) (a) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525. (b) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519. (c) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Am. Chem. Soc.* **1971**, *93*, 5301. (d) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7051. (e) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

(17) Koch, H. *Brennst. Chem.* **1955**, *36*, 321.

(18) (a) Olah, G. A. *Friedel−Crafts and Related Reactions*; Wiley-Interscience: New York, 1964. (b) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(19) Olah, G. A. In *Stable Carbocation Chemistry*; Prakash, G. K. S.; Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1997; Chapter 1.

the cationic Cu(I) or Au(I) carbonyl catalyst. For example, the yield of tertiary C7-acids is 73% with the Pt(I) carbonyl catalyst at the concentration of 0.1 M $[\{Pt(CO)_3\}_2]^{2+}$(**1**) (2 mmol PtO_2 in 10 mL 96% H_2SO_4) and at **1**/1-hexene = 1.0 mmol/5.0 mmol, being slightly lower than the 80% yield with the Au(I) carbonyl catalyst at the same concentration of 0.1 M Au^+ and at the same ratio of Au^+/1-hexene = 1.0 mmol/5.0 mmol.[8c] For comparison, the yield of the tertiary C7-acids is 80% with the Cu(I) carbonyl catalyst at the concentration of 0.4 M Cu^+ and at Cu^+/1-hexene = 1.0 mmol/5.0 mmol.[7c] When the concentration of **1** is kept at 0.1 M, the increase in the added substrate, 1-hexene, from **1**/1-hexene = 1.0 mmol/5.0 mmol to 1.0 mmol/10.0 mmol does not result in a significant change in the yield of the tertiary C7-acids, whereas the decrease in the concentration of **1** from 0.1 to 0.05 M in 96% H_2SO_4 leads to the decrease in the yield of the tertiary C7-acids from 73% to 62% due to the presence of polymerization as a competing reaction. In contrast to the high catalytic activity of **1**, *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$ (**2**) was found to have a very low catalytic activity for the carbonylation of olefins, with which tertiary C7-acids were obtained from 1-hexene in a total yield as low as 20% in 96% H_2SO_4 at room temperature and atmospheric CO pressure.



$$\text{R-CH=CH}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow[\text{1 atm, rt}]{[\{\text{Pt(CO)}_3\}_2]^{2+},\ \text{H}_2\text{SO}_4} \text{R}^1\text{-}\overset{\text{R}^2}{\underset{\text{CH}_3}{\text{C}}}\text{-COOH} \qquad (3)$$

Recently, Mogi et al. calculated the average dissociation energy for $[\{Pt(CO)_3\}_2]^{2+}$ (as one-quarter of the reaction energy for the dissociation of $[\{Pt(CO)_3\}_2]^{2+}$ (D_{2d}) to $[Pt_2(CO)_2]^{2+}$ (D_{2h}, linear)) to be 60.4 kcal/mol.[14] On the other hand, Armentrout and co-workers[20] determined the bond energies for the gas-phase complexes $(CO)M^+-CO$ to be 41 and 26 kcal/mol for M = Cu and Ag, respectively, and Veldkamp and Frenking[21] calculated (MP2 level of theory) the $(CO)M^+-CO$ bond energies to be 27 and 50 kcal/mol for M = Ag and Au, respectively. These results predicted the stability of the monovalent, metal carbonyl cations to be in the order of $[Ag(CO)_2]^+ < [Cu(CO)_2]^+ < [Au(CO)_2]^+ < [\{Pt(CO)_3\}_2]^{2+}$. The prediction is in good agreement with the experimental observations that to remove CO ligands from $[\{Pt(CO)_3\}_2]^{2+}$ requires a prolonged evacuation (ca. 1 day) of the solution of **1** whereas $[Cu(CO)_2]^+$, $[Ag(CO)_2]^+$, and $[Au(CO)_2]^+$ require only a brief evacuation (several seconds) to reversibly remove the CO ligands.[6,8] As shown in Table 1, the conversions of olefins to tertiary carboxylic acids by the platinum(I) carbonyl catalyst are comparable to those by the Cu(I), Ag(I), and Au(I) carbonyl catalysts, despite the significantly high stability of the Pt−CO bonds in the dinuclear Pt(I) carbonyl complex. The observations of the Pt(I) carbonyl catalyst conflict with the *CO carrier* model[2a,7c] and support that the coordination of the substrate to the metal, i.e., the formation of an *olefin−metal−CO* intermediate, should be involved in the reaction mechanism for the carbonylation of olefins in strongly acidic media.[8] A theoretical study (B3LYP level of theory) on the copper(I), silver(I), and gold(I) carbonyl cation-catalyzed carbonylations has indicated that the carbonylations of ethylene, propylene, and isobutene prefer to proceed via olefin−metal(I)−dicarbonyl intermediates.[22] For *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$ (**2**), the Pt−CO bonding to Pt(II) is so strong that it is difficult for the substrate to replace a CO ligand to form the olefin−Pt(II)−carbonyl intermediate, and therefore, **2** was observed to have a very low catalytic activity for the carbonylation of olefins in strong acids.

Conclusions

In summary, we have found that hexacarbonyldiplatinum(I), $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), the first homoleptic, dinuclear, cationic platinum carbonyl complex, is formed in concd H_2SO_4 solution under a CO atmosphere. The Pt−C bonding in $[\{Pt(CO)_3\}_2]^{2+}$ is much weaker than in *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$. $[\{Pt(CO)_3\}_2]^{2+}$ is the first example of the homoleptic, dinuclear, cationic metal carbonyl catalyst, which, in concd H_2SO_4 solution, catalyzes the carbonylation of olefins to give *tert*-carboxylic acids in high yields at room temperature and 1 atm of CO, whereas *cis*-$Pt(CO)_2{}^{2+}{}_{(solv)}$ has a very low catalytic activity.

Experimental Section

Commercial reagents, $PtO_2 \cdot xH_2O$ (Pt, 78.8 wt %; Mitsuwa Pure Chemicals), H_2SO_4 (96%, Kanto Chemical Co.), CO (Nippon Sanso), D_2SO_4 (96%, CIL), and ^{13}CO (^{13}C enrichment 99%, ICON) were used for the preparation and characterization of the new platinum(I) carbonyl catalyst, $[\{Pt(CO)_3\}_2]^{2+}$ (**1**), and *cis*-$[Pt(CO)_2]^{2+}{}_{(solv)}$ (**2**). Reagents (special grade, Wako Pure Chemical) 1-pentene, 1-hexene, 1-octene, 1-decene, and cyclohexene were used for the carbonylation without further purification. The preparation and characterization of **1** and **2** were carried out as previously described.[12] The carbonylation of the olefins was carried out by a method similar to that described in previous papers.[8] Using a syringe, an olefin was added dropwise into the concd H_2SO_4 solution of **1**. After the reaction was finished, the reaction mixture was poured over ice−water. The products were extracted with *n*-hexane and analyzed by GC, NMR, and IR. Identification of the products in Table 1 was carried out by a comparison of the retention times and "spiking" with the authentic samples prepared by the Cu(I) carbonyl cation-catalyzed carbonylation of olefins.

Acknowledgment. We thank Profs. B. T. Heaton, K. Kanamori, and T. Eguchi and Drs. C. Jacob, K. Mogi, and Y. Ichihashi for their valuable help and discussions. Profs. H. Willner and F. Aubke are acknowledged for a preprint of their work prior to publication. Q.X. expresses his thanks to the Society of Synthetic Organic Chemistry, Japan, for Daicel Award 1997/1998 and to Daicel Chemical Industries, LTD for financial support.

JO000883C

---

(20) Meyer, F.; Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 4071.

(21) Veldkamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613.

(22) Mogi, K.; Sonoda, T.; Sakai, Y.; Xu, Q.; Souma, Y., to be submitted for publication.